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## A Neutron Diffraction Study of $\alpha$ -Oxalic Acid Dihydrate

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A determination of the crystal structure of  $\alpha$ -oxalic acid dihydrate from three-dimensional neutron diffraction data has confirmed, with greater precision, the atomic parameters found previously from  $h0l$  and  $0kl$  data. Assumptions concerning the vibration state of the molecule are shown to introduce uncertainties in bond lengths much greater than the standard deviations derived from least-squares refinement of atomic parameters. The extent to which data collection at low temperature would reduce the uncertainty is calculated.

### Introduction

The crystal structure of  $\alpha$ -oxalic acid dihydrate (here abbreviated  $\alpha$ -POX) has been investigated several times by X-ray diffraction methods. Ahmed & Cruickshank (1953) obtained the positions of the carbon and oxygen atoms by a re-examination of earlier two-dimensional data of Robertson & Woodward (1936) and Brill, Hermann & Peters (1942). Garrett (1954) carried out a neutron diffraction investigation and located the hydrogen atoms from  $h0l$  and  $0kl$  data.

The present three-dimensional neutron structure determination has been carried out in order to obtain more precise atomic parameters (particularly for the hydrogen atoms), to examine the effects of assumptions about the atomic anisotropic thermal motions on the observed bond lengths, and to enable a more complete comparison between X-ray and neutron diffraction studies of this material ( $\alpha$ -POX, Delaplane & Ibers, 1969), and the two deuterated crystalline forms ( $\alpha$ -DOX and  $\beta$ -DOX, Coppens & Sabine, 1969).

### Experimental

The crystals of oxalic acid dihydrate were obtained from Dr A. McL. Mathieson of the Division of Chemical Physics, C.S.I.R.O., Melbourne.

The crystal data (from Delaplane & Ibers, 1969) are:

Space group  $C_{2h}^5 - P2_1/n$ ,  
 $a = 6.119$ ,  $b = 3.607$ ,  $c = 12.057$  Å,  $\beta = 106^\circ 19'$ ,  $Z = 2$ .

Two crystals were used, one of mass 36.65 mg and one of mass 2.75 mg. Most of the data were obtained from the larger crystal which was pillar shaped with well developed  $\{101\}$ ,  $\{10\bar{1}\}$  and  $\{001\}$  forms. The small crystal was cut to a rough cube.

### Data collection

The data were collected on two single-crystal diffractometers installed on the reactor HIFAR. For these instruments the respective fluxes and wave lengths of the monochromatic neutron beam at the specimen are  $2.8 \times 10^5$  n cm<sup>-2</sup> sec<sup>-1</sup> at 1.10 Å, and  $6 \times 10^6$  n cm<sup>-2</sup> sec<sup>-1</sup> at 1.09 Å.

The large crystal was mounted on a two-circle goniometer with  $c^*$  along the  $\varphi$  axis so that a  $\varphi$ -rotation would present maximum and minimum path lengths for the incident and diffracted beams of  $00l$  reflections and enable extinction and absorption effects to be detected. Both effects were apparent. However, the integrated intensities  $00l$  observed at a  $\varphi$ -setting half way between the minimum and maximum neutron path length positions were 30 per cent larger than those

observed at the minimum path length position. This effect could only be attributed to an anisotropic mosaic spread\* such that in crystal sections taken parallel to the *ab* plane, there is greater rumpling of the mosaic structure along the *b* direction than along *a*. When the smaller crystal was examined with the high flux neutron beam, the same anisotropic extinction effect was present but in this case the maximum variation in integrated intensity was only 9 per cent.

The neutron intensity data collected for  $\alpha$ -POX consisted of three subsets of data, with appropriate overlap to permit these to be placed on the same relative scale. Firstly, 708 reflections were measured from the large crystal with the low flux beam; of these, 90 were rejected

because of severe extinction and 209 were not above background. Secondly, the weak reflections were re-measured from the large crystal with the high flux beam; the number of unobservably weak reflections was reduced to 119. Thirdly, the 90 reflections rejected from the first data were re-measured from the small crystal with the high flux beam. No attempt was made to correct these data for extinction effects.

For the intensity measurements the diffractometers were operated by step scanning in the  $\theta:2\theta$  mode controlled by monitor counters. The numbers of counts per step ( $3'$  of  $2\theta$ ) were punched on paper tape. The length of the scan was such that the peak occupied the central third of the  $2\theta$  range. In extracting the intensities the background was taken as close as possible to the peak in order to make an empirical allowance for diffuse scattering at and around the Bragg position.

\* A similar observation was made by Delaplane & Ibers (1969) in their X-ray study of  $\alpha$ -POX.

Table 1. Observed and calculated structure factors (*f* units)

Asterisks mark unobservably weak reflections. Columns are: *l* index,  $|F_{\text{obs}}|$ ,  $F_{\text{calc}}$ .

<i>l</i>	$ F_{\text{obs}} $	$F_{\text{calc}}$	<i>l</i>	$ F_{\text{obs}} $	$F_{\text{calc}}$	<i>l</i>	$ F_{\text{obs}} $	$F_{\text{calc}}$
0	0	0	211	-7	158	159	2	14*
1	184	170	212	-7	140	158	3	11*
2	398	355	213	-7	40	31	3	98
3	134	123	214	-7	37	31	3	86
4	366	312	215	-7	68	53	4	62
5	504	452	216	-7	46	46	4	60
6	453	433	217	-7	15	15	4	166
7	67	67	218	-7	169	169	5	188
8	126	111	219	-7	5	5	5	188
9	195	200	220	-7	106	64	5	113*
10	14	4	221	-7	106	64	5	38
11	14	4	222	-7	224	242	5	213
12	66	67	223	-7	224	242	5	137
13	16	16	224	-7	60	53	6	97
14	195	200	225	-7	20	20	6	36
15	14	4	226	-7	172	154	6	27
16	14	4	227	-7	14	14	6	36
17	14	4	228	-7	14	14	6	36
18	14	4	229	-7	14	14	6	36
19	14	4	230	-7	14	14	6	36
20	14	4	231	-7	14	14	6	36
21	14	4	232	-7	14	14	6	36
22	14	4	233	-7	14	14	6	36
23	14	4	234	-7	14	14	6	36
24	14	4	235	-7	14	14	6	36
25	14	4	236	-7	14	14	6	36
26	14	4	237	-7	14	14	6	36
27	14	4	238	-7	14	14	6	36
28	14	4	239	-7	14	14	6	36
29	14	4	240	-7	14	14	6	36
30	14	4	241	-7	14	14	6	36
31	14	4	242	-7	14	14	6	36
32	14	4	243	-7	14	14	6	36
33	14	4	244	-7	14	14	6	36
34	14	4	245	-7	14	14	6	36
35	14	4	246	-7	14	14	6	36
36	14	4	247	-7	14	14	6	36
37	14	4	248	-7	14	14	6	36
38	14	4	249	-7	14	14	6	36
39	14	4	250	-7	14	14	6	36
40	14	4	251	-7	14	14	6	36
41	14	4	252	-7	14	14	6	36
42	14	4	253	-7	14	14	6	36
43	14	4	254	-7	14	14	6	36
44	14	4	255	-7	14	14	6	36
45	14	4	256	-7	14	14	6	36
46	14	4	257	-7	14	14	6	36
47	14	4	258	-7	14	14	6	36
48	14	4	259	-7	14	14	6	36
49	14	4	260	-7	14	14	6	36
50	14	4	261	-7	14	14	6	36
51	14	4	262	-7	14	14	6	36
52	14	4	263	-7	14	14	6	36
53	14	4	264	-7	14	14	6	36
54	14	4	265	-7	14	14	6	36
55	14	4	266	-7	14	14	6	36
56	14	4	267	-7	14	14	6	36
57	14	4	268	-7	14	14	6	36
58	14	4	269	-7	14	14	6	36
59	14	4	270	-7	14	14	6	36
60	14	4	271	-7	14	14	6	36
61	14	4	272	-7	14	14	6	36
62	14	4	273	-7	14	14	6	36
63	14	4	274	-7	14	14	6	36
64	14	4	275	-7	14	14	6	36
65	14	4	276	-7	14	14	6	36
66	14	4	277	-7	14	14	6	36
67	14	4	278	-7	14	14	6	36
68	14	4	279	-7	14	14	6	36
69	14	4	280	-7	14	14	6	36
70	14	4	281	-7	14	14	6	36
71	14	4	282	-7	14	14	6	36
72	14	4	283	-7	14	14	6	36
73	14	4	284	-7	14	14	6	36
74	14	4	285	-7	14	14	6	36
75	14	4	286	-7	14	14	6	36
76	14	4	287	-7	14	14	6	36
77	14	4	288	-7	14	14	6	36
78	14	4	289	-7	14	14	6	36
79	14	4	290	-7	14	14	6	36
80	14	4	291	-7	14	14	6	36
81	14	4	292	-7	14	14	6	36
82	14	4	293	-7	14	14	6	36
83	14	4	294	-7	14	14	6	36
84	14	4	295	-7	14	14	6	36
85	14	4	296	-7	14	14	6	36
86	14	4	297	-7	14	14	6	36
87	14	4	298	-7	14	14	6	36
88	14	4	299	-7	14	14	6	36
89	14	4	300	-7	14	14	6	36
90	14	4	301	-7	14	14	6	36
91	14	4	302	-7	14	14	6	36
92	14	4	303	-7	14	14	6	36
93	14	4	304	-7	14	14	6	36
94	14	4	305	-7	14	14	6	36
95	14	4	306	-7	14	14	6	36
96	14	4	307	-7	14	14	6	36
97	14	4	308	-7	14	14	6	36
98	14	4	309	-7	14	14	6	36
99	14	4	310	-7	14	14	6	36
100	14	4	311	-7	14	14	6	36
101	14	4	312	-7	14	14	6	36
102	14	4	313	-7	14	14	6	36
103	14	4	314	-7	14	14	6	36
104	14	4	315	-7	14	14	6	36
105	14	4	316	-7	14	14	6	36
106	14	4	317	-7	14	14	6	36
107	14	4	318	-7	14	14	6	36
108	14	4	319	-7	14	14	6	36
109	14	4	320	-7	14	14	6	36
110	14	4	321	-7	14	14	6	36
111	14	4	322	-7	14	14	6	36
112	14	4	323	-7	14	14	6	36
113	14	4	324	-7	14	14	6	36
114	14	4	325	-7	14	14	6	36
115	14	4	326	-7	14	14	6	36
116	14	4	327	-7	14	14	6	36
117	14	4	328	-7	14	14	6	36
118	14	4	329	-7	14	14	6	36
119	14	4	330	-7	14	14	6	36

## Analysis of data

## 1. Absorption correction

Absorption effects in hydrogen-containing crystals are due to the high incoherent scattering cross-section of hydrogen. In making a correction there is an uncertainty about the appropriate value of this cross section. The free atom cross-section for hydrogen is 20 barns while application of the usual relationship between free and bound cross sections predicts  $\sigma_{\text{bound}}$  to be 80 barns. For neutrons of the wavelength used in these experiments the cross section lies between these values since

an indeterminate but appreciable energy interchange takes place. The appropriate incoherent cross-section was chosen to be that of hydrogen in water which was measured as 34 barns at the neutron energies used in this work. This value agrees with that of Melkonian (1949). The observed intensities were corrected by numerical integration over the neutron path length in the crystal.

## 2. Weighting the data

It was realized that basing the weight on the statistical errors alone would give an unrealistically high

Table 2. Fractional positional and thermal parameters of all atoms with their standard deviations

Thermal parameters are in the form  $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .  
All parameters and e.s.d.'s are expressed  $\times 10^4$ .

	$x, \sigma(x)$	$y, \sigma(y)$	$z, \sigma(z)$	$\beta_{11}, \sigma(\beta_{11})$	$\beta_{22}, \sigma(\beta_{22})$	$\beta_{33}, \sigma(\beta_{33})$	$\beta_{12}, \sigma(\beta_{12})$	$\beta_{13}, \sigma(\beta_{13})$	$\beta_{23}, \sigma(\beta_{23})$
C(1)	-452 (2)	547 (4)	510 (1)	169 (4)	462 (11)	27 (1)	49 (4)	21 (1)	1 (2)
O(1)	847 (4)	-599 (6)	1488 (2)	228 (6)	827 (18)	29 (1)	143 (7)	19 (2)	7 (3)
O(2)	-2197 (3)	2310 (6)	360 (2)	224 (6)	838 (17)	32 (1)	184 (7)	26 (2)	7 (3)
O(3)	-4509 (4)	6136 (6)	1799 (2)	219 (6)	829 (17)	33 (1)	69 (8)	31 (2)	22 (3)
H(1)	293 (7)	93 (12)	2189 (3)	285 (10)	945 (29)	45 (2)	58 (14)	32 (4)	4 (6)
H(2)	-5740 (7)	6864 (13)	1142 (3)	314 (12)	1083 (35)	50 (3)	105 (17)	24 (4)	47 (7)
H(3)	-3599 (9)	4447 (14)	1508 (4)	343 (13)	1097 (40)	79 (3)	126 (19)	66 (5)	15 (9)

Table 3. Bond lengths for  $\alpha$ -POX and  $\alpha$ -DOX

The e.s.d.'s given in brackets refer to the least significant digits in the bond lengths.

	$\alpha$ -POX This investigation (neutron)	$\alpha$ -POX Ahmed & Cruickshank (X-ray)	$\alpha$ -POX Garrett (neutron)	$\alpha$ -POX Delaplane & Ibers (X-ray)	$\alpha$ -DOX Coppens & Sabine (neutron)
C(1)-C(1)	1.536 (3) Å	1.529 (20) Å	1.533 (11) Å	1.538 (2) Å	1.539 (2) Å
C(1)-O(1)	1.291 (5)	1.285 (12)	1.254 (8)	1.285 (1)	1.291 (2)
C(1)-O(2)	1.212 (4)	1.187 (22)	1.229 (14)	1.212 (1)	1.208 (2)
O(1)-H(1)	1.026 (7)		1.057 (16)		1.031 (2)
O(3)-H(2)	0.964 (7)		0.968 (29)		0.954 (2)
O(3)-H(3)	0.956 (9)		0.945 (21)		0.954 (2)
H(1)···O(3 <sup>iii</sup> )	1.480 (7)				1.493 (2)
H(2)···O(2 <sup>iii</sup> )	1.917 (8)				1.939 (2)
H(3)···O(2 <sup>iv</sup> )	1.979 (9)				2.008 (2)
O(1)···O(3 <sup>ii</sup> )	2.506 (4)	2.491 (8)	2.518 (8)	2.512 (1)	2.524 (2)
O(3)···O(2 <sup>iii</sup> )	2.864 (5)	2.879 (9)		2.864 (2)	2.879 (2)
O(3)···O(2 <sup>iv</sup> )	2.881 (4)	2.885 (18)		2.883 (1)	2.906 (2)

Table 4. Bond angles for  $\alpha$ -POX and  $\alpha$ -DOX

The e.s.d.'s given in brackets refer to the least significant digits in the bond angles.

	$\alpha$ -POX This investigation (neutron)	$\alpha$ -POX Ahmed & Cruickshank (X-ray)	$\alpha$ -POX Garrett (neutron)	$\alpha$ -POX Delaplane & Ibers (X-ray)	$\alpha$ -DOX Coppens & Sabine (neutron)
O(1)-C(1)-O(2)	126.6 (3)°	125.8 (14)°	126.7 (9)°	126.8 (1)°	126.6 (1)°
O(1)-C(1)-C(1 <sup>i</sup> )	112.4 (3)	112.6 (10)	112.3 (7)	112.1 (1)	112.2 (1)
O(2)-C(1)-C(1 <sup>i</sup> )	121.0 (3)	121.6 (11)	120.9 (8)	121.1 (1)	121.2 (1)
C(1)-O(1)-H(1)	114.4 (6)				112.8 (1)
H(2)-O(3)-H(3)	105.9 (7)		105.8 (17)		105.8 (2)
O(1)-H(1)···O(3)	179.3 (6)		175.3 (20)		177.4 (1)
H(1)···O(3)-H(2)	112.8 (7)		112.9 (30)		113.7 (1)
H(1)···O(3)-H(3)	116.8 (4)				116.8 (1)
O(3)-H(2)···O(2 <sup>iii</sup> )	166.9 (6)				167.7 (2)
H(2)···O(2 <sup>iii</sup> )-C(1 <sup>iii</sup> )	122.8 (6)				123.1 (1)
O(3)-H(3)···O(2 <sup>iv</sup> )	156.6 (7)		156.1 (30)		156.0 (2)
H(3)···O(2 <sup>iv</sup> )-C(1 <sup>iv</sup> )	129.5 (7)				129.6 (1)

weight to the intense reflections and so the standard deviation of an observed structure amplitude was assumed to be

$$\sigma(F) = \sigma + 0.05|F|$$

where  $\sigma$  is the estimated standard deviation based on counting statistics.

The unobservably small structure amplitudes were assigned values of  $0.4 F_{\min}$  with e.s.d.'s of  $0.2 F_{\min}$  where  $F_{\min}$  is the minimum observable value of a structure amplitude at the corresponding Bragg angle.

### 3. Structure refinement

The structure parameters were refined and interpreted using the computer programs *ORFLS* and *ORFFE* (Busing, Martin & Levy, 1962*a, b*). The initial parameters were those found by Baur (private communication) from a re-analysis of Garrett's data. The scattering lengths were set at  $O = 5.8 f$ ,  $C = 6.61 f$  and  $H = -3.78 f$ .<sup>\*</sup> An overall scale factor and the positional parameters and anisotropic temperature factors for each atom were varied. The refinement was based on  $F$  and each reflection was weighted according to the standard deviations found above.

The final discrepancy factors were:

- (1)  $R$  including all reflections, 0.083 ;
- (2)  $R$  omitting unobserved reflections, 0.072 ;
- (3) Weighted  $R$ , omitting unobserved reflections, 0.092 .

In Table 1 the calculated and observed structure factors are compared. Table 2 gives the positional and thermal parameters for each atom with their standard deviations.

## Discussion

### 1. Bond lengths and bond angles

Bond lengths and bond angles are shown in Tables 3 and 4 together with the corresponding values found for  $\alpha$ -POX by other investigators and for  $\alpha$ -DOX by Coppens & Sabine (1969).

The present neutron results for the carbon and oxygen atom configuration in the  $\alpha$ -POX structure agree with the X-ray results within experimental error, thus helping to confirm the observations of Delaplane & Ibers (1969), that there are no significant differences in the heavier atom geometry of the oxalic acid molecule in  $\alpha$ -POX and  $\alpha$ -DOX and that the major effects of deuteration are in the significant lengthening of the O...O distances in all three hydrogen bonds.

A comparison of our neutron results for  $\alpha$ -POX with those of Coppens & Sabine (1969) for  $\alpha$ -DOX shows good agreement between the proton and deuteron intramolecular configurations, e.g. the covalent bond lengths involving hydrogen atoms and the bond angle in the water molecule are the same within experimental error. However, the bond angle C—O(1)—H(1) shows a de-

crease ( $1.6^\circ$ ) on deuteration, which is possibly significant in terms of its e.s.d. ( $0.6^\circ$ ).

It is interesting to note that isotopic substitution has no effect, within experimental error, on the angular relationships at the hydrogen atoms in the two longer hydrogen bonds. Deuteration results simply in lengthening the H(2)...O(2<sup>iii</sup>) and H(3)...O(2<sup>iv</sup>) distances by 0.022 and 0.029 Å, with e.s.d. 0.009 Å in both cases. The corresponding lengthenings of O...O distances are 0.015 and 0.025 Å with e.s.d.'s of 0.006 and 0.005 Å respectively. In the short hydrogen bond, the isotope effect may be more complex, since, in addition to a slight but significant increase in O(1)...O(3<sup>ii</sup>) distance (0.018 Å with e.s.d. of 0.005 Å) deuteration results in a possibly significant bending ( $1.9^\circ$  with e.s.d. of  $0.6^\circ$ ) in the angle O(1)—H(1)...O(3<sup>ii</sup>). This is associated with the decrease in C—O(1)—H(1) angle described above.

### 2. Thermal parameters

Each bond length in  $\alpha$ -POX is subject to a correction which is uncertain, to the extent that it depends on assumptions as to the relative thermal vibrational behaviour of the atoms involved. The small differences in atomic configuration between  $\alpha$ -POX and  $\alpha$ -DOX will not be greatly affected in this way because the vibrational behaviour in the two crystal structures should be very similar. However, in Table 5, it is shown that the two sets of bond lengthenings introduced by assuming the riding and the independent modes of thermal motion (Busing, & Levy, 1964) may in some bonds differ by an order of magnitude greater than the e.s.d.'s in the uncorrected bond lengths.

Table 5. Bond lengths corrected for thermal motion

- (1) Separation of mean positions of atoms with e.s.d.
- (2) Corrected for thermal motion assuming second atom riding on first.
- (3) Corrected for thermal motion assuming independent thermal motion.

	(1)	(2)	(3)
C(1)—C(1)	1.536 (5) Å	1.536 Å	1.571 Å
C(1)—O(1)	1.291 (5)	1.304	1.349
C(1)—O(2)	1.212 (4)	1.227	1.276
O(1)...O(3)	2.506 (5)	2.506	2.542
O(1)—H(1)	1.026 (7)	1.034	1.132
O(3)—H(3)	0.956 (9)	0.986	1.066
O(3)—H(2)	0.964 (7)	0.985	1.074
O(3)...H(1)	1.480 (7)	1.486	1.546

The 'riding' correction is probably a good approximation for the water molecule O—H bond lengths, since this assumes that the center of vibration of the hydrogen atoms is relative to the instantaneous position of the oxygen atom. The 'independent' correction is probably more appropriate for the intermolecular distances. Calculations assuming a rigid body motion of the oxalic acid molecule in  $\alpha$ -DOX (Coppens & Sabine, 1969) predict bond length corrections similar to our riding corrections for  $\alpha$ -POX.

\* 1 f = 1 fermi =  $10^{-15}$  meter.

It is desirable to reduce the bond length corrections by collecting the intensity data at low temperature. Calculations based on the equations below indicate the improvement to be expected. Let the atomic mean square vibration amplitudes  $\bar{u}^2$  be given by

$$\bar{u}^2 = \frac{3h^2T}{4\pi^2mk\theta_M^2} \left\{ \varphi(x) + \frac{x}{4} \right\},$$

where  $m$  is the mass of the atom and  $\theta_M$  the Debye temperature determined by diffraction methods, and

$$\varphi(x) = \frac{1}{x} \int_0^x \frac{\xi d\xi}{\exp(\xi) - 1},$$

where  $x = \theta_M/T$ .

The two possible approximations to the real situation are:

(i) The crystal is best described by an overall Debye temperature.

or,

(ii) A separate Debye temperature should be assigned to each atom.

Calculations for both these conditions have been carried out. On assumption (i), the overall Debye temperature is 141°K.

The experimentally determined thermal ellipsoid were reduced by  $(\bar{u}_{77^\circ\text{K}}^2)/(\bar{u}_{298^\circ\text{K}}^2)$  and  $(\bar{u}_{4^\circ\text{K}}^2)/(\bar{u}_{298^\circ\text{K}}^2)$  and the thermal corrections to the bond lengths were then recalculated (Table 6). If assumption (i) is correct there is an advantage in reducing the temperature to 4°K; however, if (ii) is better, it is worthwhile to go to 77°K but there is no substantial gain in working at 4°K.

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Table 6. *Variation in bond length corrections with temperature*

$\Delta L$  is the calculated difference between the bond corrections assuming riding and independent thermal motions. (1) is the bond length difference when an overall Debye temperature is assumed, (2) the difference when individual atomic Debye temperatures are used.  $\sigma$  is the e.s.d. in the uncorrected bond length.

	Temperature (°K)	$\Delta L$		$\sigma$
		(1)	(2)	
C(1)—C(1 <sup>1</sup> )	77	0.010 Å	0.015 Å	0.005 Å
	4	0.004	0.012	
C(1)—O(1)	77	0.012	0.017	0.005
	4	0.005	0.014	
C(1)—O(2)	77	0.012	0.017	0.004
	4	0.005	0.013	
O(1)···O(3)	77	0.009	0.011	0.005
	4	0.003	0.011	
O(1)—H(1)	77	0.023	0.027	0.007
	4	0.009	0.026	
O(3)—H(2)	77	0.022	0.027	0.007
	4	0.009	0.019	
O(3)—H(3)	77	0.021	0.026	0.009
	4	0.009	0.018	
O(3)···H(1)	77	0.016	0.019	0.007
	4	0.007	0.013	

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